CERTIFICATION OF APPROVAL

A Study on Adsorption of Fe (II) Ion by Rice Husks Digested with Nitric Acid

by

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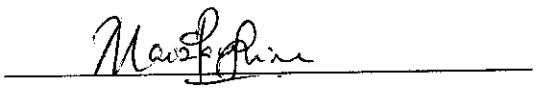

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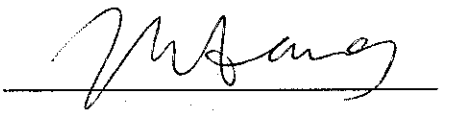

HAIDAR ZHAFRI BIN HOSEN

ABSTRACT

The objective of this study is to produce activated carbon from rice husks for Fe(II) ion adsorption. Rice husks were digested by nitric acid at different concentrations at ambient temperature over a period of 4 – 12 hours. The adsorption uptake increased with the increase of the nitric acid concentration and digestion time due to higher microporosity and larger internal surface. The carbonization temperature was varied to 500°C and 700 °C. The optimum carbonization temperature was identified to be 700 °C. Using data supplied by the Atomic Absorption Spectrometry, adsorption isotherms were structured. The adsorption characteristics followed the Langmuir isotherms.

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INTRODUCTION

1.1 Background of Work

In Malaysia, 200 kg of rice husk is gained from every tonne of rice produced. The amount of the rice husk waste gained is reaching up to 3.6 million tonne per year. Thus there is a need to figure up ways to utilize this waste rather than totally disposing it. Due to its availability and large amount, rice husks are relatively cheap which made it suitable to satisfy the purpose of this research.

Rice husk is an abrasive thin layer of rice skin which covered the edible rice kernel. It is mainly consist of hemi cellulose, lignin, cellulose, yet rich in silica content. It contains a high percentage of organic substances, as does other plant biomass; therefore it is recognized as a potential source of energy and organic chemicals. Combustion, pyrolysis, and gasification processes of rice husks have been developed to generate heat and/or electrical power. Also, material conversion technologies for converting rice husk into useful chemicals e.g. saccharides, and furfurals, have been investigated [1]. On the other hand, the high content of silicon, approximately 15 – 20 % as SiO_2 is also considered as an essential feature of rice husk. In fact, many applications of rice husk silica have been reported, focusing on a wide variety of products, e.g. metallurgical silicon, ceramics, zeolites, silicon tetrachloride, and cement/concrete applications [1].

In this research, iron (Fe^{2+}) ion is chosen specifically for the adsorption test since these cations are commonly found in the industrial waste. Iron (Fe) is an essential ion for the production of red blood cells in human's body. It exists in the hemoglobin that is responsible for carrying oxygen around the blood stream. Iron deficiency leads to anemia. Nonetheless all iron compounds should be regarded as toxic. Excess iron in the body could causes liver and kidney damage (haemochromatosis) while some iron

compounds are suspected carcinogens which could initiate cancer cell growth in human's body. From the environmental aspect, iron could cause considerable damages. For example iron could impart unpleasant dingy look and rust colored stain to home equipments and to the surroundings.

As the activating agent chosen for the topic, nitric acid is an exceedingly strong acid which contain a high proportion of hydrogen ion. Its degree of dissociation, like other strong electrolytes, is regarded as doubtful. It displays the normal properties of an acid in all cases where its oxidizing action does not come into play. Thus it reacts with basic oxides, hydroxides, and carbonates in the usual way unless the metallic radical has reducing properties for example ferrous or stannous compounds [2].

Liquid nitric acid is not obtainable in stage of complete purity. Owing to a slight degree of decomposition which always takes place, even below boiling point, the purest acid is colorless fuming liquid which is obtained upon distillation of a strong solution under reduced pressure with concentrated sulfuric acid and ozone [2]. It has a density of 1.41 and molecular weight of 63.02. The odor of nitric acid is from sweet to pungent. In liquid state, it may rapidly attacks flesh and most organic matter. As gaseous oxides it acts anesthetically to dangerously toxic. Therefore, extra precautions steps have to be taken in dealing with nitric acid due to the hazards it may cause.

1.2 Problem Statement

The presence of heavy metals in environment caused hazards to human's health and environment. The main source of the heavy metals is from the waste water disposed by the industrial and mining site. These days, the increasing awareness of the environmental effect from the heavy metals has led to the enforcement of more stringent water quality legislation such as the Environmental Quality (Scheduled Wastes) Regulation 1989.

The enforcement of the law had affected industries that are related to metal especially for the small and medium scale industries where the expertise in wastewater treatment is unavailable. The conventional method used such as ultrafiltration, ion exchange, and electrochemical deposition are relatively high in cost which made them not economically feasible to be applied in the small scale industries. So this issue has triggered the need to search for cheaper alternatives that is more effective and economically feasible that can be adopted by such industries.

In wastewater treatment, the adsorption process is effective in removal of heavy metals at trace level. One of the best alternatives is to use activated carbon which can selectively remove metal ions from the waste water stream. Activated carbon is produced from a wide variety of carbon rich materials such as wood, coal, coconut shells, nut shells and fruit stones. Most of the materials stated are most likely to be originated from the agricultural side. Considering Malaysia as an agricultural country, the best option regarding this matter is to try to make full use of deposits from the agro industries as the source of this research. The availability of the agricultural waste in Malaysia provides wide variety options of the activated carbon source. Currently, there were studies conducted by researchers all around the country on converting the agricultural waste to be beneficial products. Hence as a part of it, this study is done specifically on determining the best way to prepare activated carbon from rice husks.

CHAPTER 2
LITERATURE REVIEW

2.1 Adsorption of Activated Carbon

Adsorption is a separation process when one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent. Adsorbent refers to small particles which adsorb the material to be recovered (adsorbate). One of the most common adsorption applications in liquid phase is the removal of organic compounds and impurities from water in water treatment. While the example of adsorption applications for the gas-phase is the dehydration of air. The adsorbents are physically in the form of small pellets, beads, and granules (0.1mm to 12 mm). The structure of the adsorbents are porous, which are divided into macro pore (>500 A), meso pore (20 – 500 A) and micro pore (<20A). Adsorbent appears in different shapes such as spheres, cylindrical pellets, flakes and powders. It has specific surface area ranged from 300 to 1,200 m^2/g.

The adsorption process occurs when the solute (adsorbate) diffuses from bulk fluid to exterior surface of adsorbent. The solute (adsorbate) is then diffuses inside the pore where finally the solute will be absorbed on the surface of the pore. The adsorbate is attached to the adsorbent by two means which are the physical adsorption using van der Waals attraction and the also chemisorptions by activated adsorption. The physical (van der Waals) adsorption occurs when the intermolecular attractive forces between molecules of a solid (adsorbent) and the gas (adsorbate) are greater than those between molecules (adsorbate) itself. For the chemisorptions (activated adsorption), the separation occurs due to formation of chemical bonds between adsorbate and adsorbent.

These are the criteria for a good adsorbent:

(i) High selectivity to enable sharp separations.
(ii) High capacity to minimize the amount adsorbent needed.
(iii) Favorable kinetic and transport properties for rapid sorption.
(iv) Chemical and thermal stability to preserve the amount and its properties.
(v) Hardness and mechanical strength
(vi) High fouling resistance
(vii) Capability of being regenerated at relatively low cost.

2.2 Preparing Activated Carbon from Rice Husks

Activated carbon is produced from carbon-rich raw materials. Currently activated carbon is manufactured from wood, coal, coconut shell and peat. Regarding to the availability of rice husks in Malaysia, it is chosen as the material to be studied as the raw material source of activated carbon. Generally, any organic materials which have large percentage of carbon are capable to be activated, hence will increase the material's sorptive characteristics. However in order to get a good activated carbon, several material characteristics are taken into accounts which are:

- High adsorptive capability
- The ability to maintain its properties under usage condition
- Have long storage life

Mainly there are two steps to prepare the activated carbon which are the activation and carbonization steps. Even though all carbon based material is able to be transformed to be activated carbon, the final product of the activated carbon will be different depending on the parameters set during the preparation steps. The nature of the raw material used and the agent raw material also play important role on affecting the final characteristics of the activated carbon prepared.

2.2.1 Activation Steps

The activation of a carbon material increases the volume and enlarges the diameters of the pores of the carbon. Initially the aromatic sheets of the carbon exposed to the action of activation agents which will leads to the development of microporous structure. Further on, the latter effect is the widening of the existing pores in the carbon and the formation of large sized pores by the complete burnout of the walls between the adjacent pores. This effect initiate the increment of the transitional pores and the macroporosity, where else decreases the volume of the micropores. The degree of the activation can be indicated by the extent of the carbon material's burnoff. Dubinin and Zaverina stated that a microporous active carbon is produced when the degree of burnoff is less than 50% and a macroporous active carbon were produced when the extent of burnoff is greater than 75%. Therefore to get an activated carbon product which has a mixed porous structure and contain all types of pores the degree of burnoff is between 50% and 75% [3].

The intermediate carbonized products which are formed by activation have carbon atoms that differ from each other in its reactivity based on their spatial arrangement. The carbon atoms which are located at the edges and periphery of the aromatic sheets or those located at defect positions and dislocations or discontinuities are associated with unpaired electrons or have residual valencies which are rich in potential energy [3]. As a result, these carbon atoms are more reactive and have a tendency to form surface compounds by oxidation. Later these will break down and peel off the oxidized carbon from the surface as gaseous oxides leaving behind new unsaturated carbon atoms for further reaction with the activating agent. [3]

2.2.2 Carbonization Steps

In the carbonization step, most of the non-carbon elements in the activated carbon like oxygen and hydrogen are eliminated as volatile gaseous products. The residual carbon atoms group themselves into sheets of condensed aromatic ring systems with a certain degree of planar structure. The irregularity of the mutual arrangement of the aromatics sheets leaves free interstices between the aromatic sheets which may be filled with the tarry matter or the products of decomposition or at least blocked partially by the disorganized carbon. These interstices increase the pores total, which make activated carbons excellent adsorbents [4].

2.3 Factors Affecting Physical Adsorption

There are several factors that will affect the adsorption rate of the activated carbon. Back to the objective of this project which is to prepare a good activated carbon, these factors should be taken into account. Thus the right parameters could be set up during the sample preparation steps and during the adsorption experiments. The factors are:

i. Activation Effect

The structure of the carbon materials is much influenced by the activation process. In this step, the activating agent (nitric acid) erodes the internal surfaces of the carbon thus develops an extensive and fine network of pores in the carbon. This oxidation process changes the surface atoms to specific chemical forms which have selective adsorption capabilities. The digestion of the rice husks with nitric acid will produce gaseous species that creates pores in the carbon (rice husks). The total time period of the rice husks digested in nitric acid is called the activation time. This activation time is a vital variable to determine the activated carbon properties.

Longer activation time will permit the acid to create more pores in the carbon; hence will increase its internal surface area. However if the activation time is too long, the

pores created are too large or too much and will make the support of the activated carbon to be unstable. When this happened, the activated carbon structures will disintegrate and break. Thus the activated carbon will have less mechanical strength to withstand the adsorption process. In addition, as the size of the pores increases to a certain extent which is too large, the total internal surface area of the activated carbon will decrease. The larger pores also could affect the adsorption process where the undesired material could be adsorbed along.

ii. Carbonization Effect

The purpose of carbonizing the activated carbon is to impart thermal decomposition to it thus eliminating non-carbon species and fixed the carbon mass as well as the basic carbon structure. Generally the quality and yield of the carbonized activated carbon are affected by several parameters which are:

(i) The rate of heating
(ii) The heating final temperature
(iii) The soaking time at the final temperature
(iv) Nature and physical state of the raw material

Low heating rate during pyrolysis results in lower volatilization and higher char yield due to increased dehydration and better stabilization of the polymeric components [4]. At the first stage of the carbonization, the structure of the activated carbon is made of small planar aromatics rings which are randomly oriented. As the heat treatment temperature increases, the random structure will start to be arranged in parallel. The basic microstructure was formed by 500°C, although some of these pores were blocked by the pyrolysis products and could be available only when high temperature treatments was given [4].

iii. Solute Nature

The polarity of the solute has intense effect of its adsorptive capability. In certain highly dissociated solutes such as sodium chloride and potassium chloride, the tendency to be adsorbed are less compared to non dissociating solutes like iodine and mercury chloride which are well adsorbed. Most of the carbon surface exhibits hydrophobic characteristics that is non polar. The hydrophobic reactions originate from the net repulsion between the water and non-polar region of the carbon surface as well as the non-polar moieties of the solute [5]. As a consequence of these repulsive interactions and high cohesive energy of water, the non-polar molecules and non-polar regions of the surface can associate when they are close proximity to each other. So it can be concluded that in aqueous systems, non-polar solutes are more strongly adsorbed than polar solutes. [5]

iv. Pore Structure of the Adsorbent

Pore structures of an activated carbon plays important role to determine the adsorbent molecules selectivity. These pore structures which has various size from 10 to 100,000Å control the sizes of molecules accessible to them.

v. Surface Chemistry

Specific functional groups on the adsorbent surface which have certain characteristics affect the adsorption process. The formation of polar surface group of chemisorbed oxygen during the activation process of activated carbon affects the adsorptive capacity for many solutes. Surface oxides consisting of acidic functional groups reduce the capacity of carbon adsorption of many organic solutes such as oxalic and succinic acid. This was attributed to the preferential adsorption of water and hence blockage of a part of the surface. While the abundance of surface oxides consisting of carbonyl group enhances the adsorption of such aromatics solutes such as phenol and naphthalene [4]

vi. Temperature

Higher environment temperature will decrease the adsorption rate. It is because higher temperature wills generates greater vibration energy to the adsorbed molecules and will make it more likely to desorb from the surface. Regarding this matter, it is recommended to place the sample in ambient temperature under isothermal condition during the adsorption steps.

vii. Surface Area of Adsorbent

Generally, the larger the surface area of the activated carbon, the higher adsorption capacity it has. Proper steps should be taken during the activation steps to ensure that the internal surface area of the carbon is activated adequately.

2.4 Properties and Structure of Activated Carbon

The properties of a good activated carbon are referred to:

(i) Its large surface area
(ii) A high degree of surface reactivity
(iii) Universal adsorption effect
(iv) Favorable pore size as an access route to the internal surfaces
(v) Enhanced mechanical strength

The commercial active carbons have a specific surface area ranged between 800 – 1500 m^2/g. The structure of the adsorbents are made up by a complex network of pores, which are divided into macro pore (diameters >50 nm), meso pore (diameters 2 – 50 nm) and micro pore (diameters <2 nm). However, the surface area is mainly made of micropores. The macropores do not contribute much toward the surface area but acts as a route of the adsorbate into the interior meso and micro pores where most adsorption takes place.

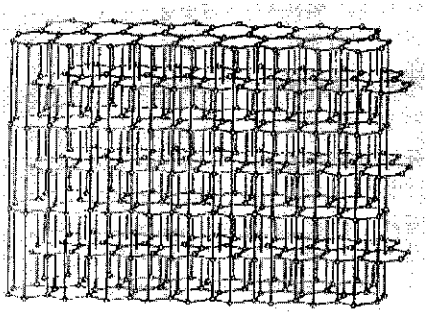
The large surface area of the activated carbon is as an upshot from the activation process where carbonaceous char with little internal surface is oxidized in an atmosphere of air, carbon dioxide or steam at a temperature between 800 °C and 900 °C. This makes the oxidation of some of the regions within the char in preference to others so that as combustion proceeds a preferential etching occurs, resulting the development of a large internal surface area, which can be as high as 2500 m^2/g. [3]

The structure of a carbonaceous material is closely linked with the porosity of the material. The building block in carbons is primarily graphitic sheets, which are characterized by strong covalent bonding between the basal planes. Yet the structure of activated carbon is thought to be composed of micro crystallites with a structure similar to graphite [6].

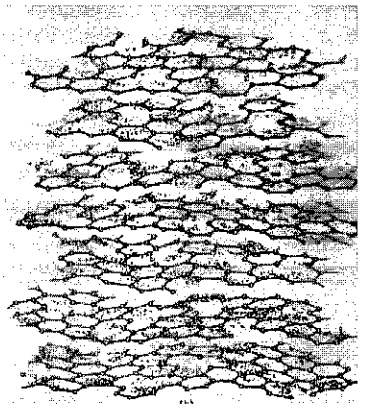
2.4.1 Physical Characteristics of Activated Carbons

Figure 1 illustrates the structures of graphite (a) and turbostratic carbon (b). Activated carbons are similar to the latter type, having microcrystallites only a few layers in thickness and less than 100 Å in width. The level of structural imperfections in activated carbon microcrystallites is very high, which results in many possibilities for reactions of the edge carbons with their surroundings [7].

Figure 1: Schematic Diagram comparing (a) a three dimensional graphite lattice with (b) a turbostratic structure



(a)



(b)

Activated carbons owe a large portion of their remarkable adsorption properties to their porous nature. Figure 2 for example is a scanning electron photomicrograph of a sample carbon which is a particularly good example of this porous characteristic. This is an activated carbon purposely prepared so as to induce a very high degree of transition pore porosity for increasing the diffusion-limited rate of adsorption from solution. The pores observed in Figure 2 are about 0.1 – 0.5 μ in diameter. A granule of a less porous carbon is shown in Figure 3 for comparison. It is important to point out that the physical parameters such as porosity can be controlled to some degree to produce carbons suited for special applications [7].

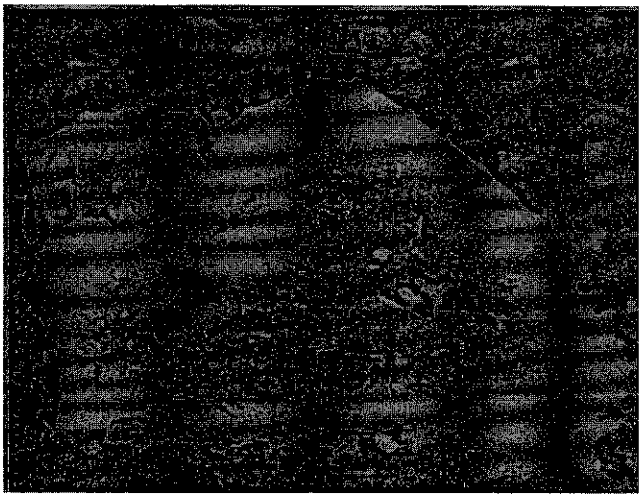


Figure 2: Scanning electron photomicrograph of an activated carbon of an activated carbon surface showing highly developed porosity in the "macroporous" range. Area shown is 15.8 x 12.5 μ

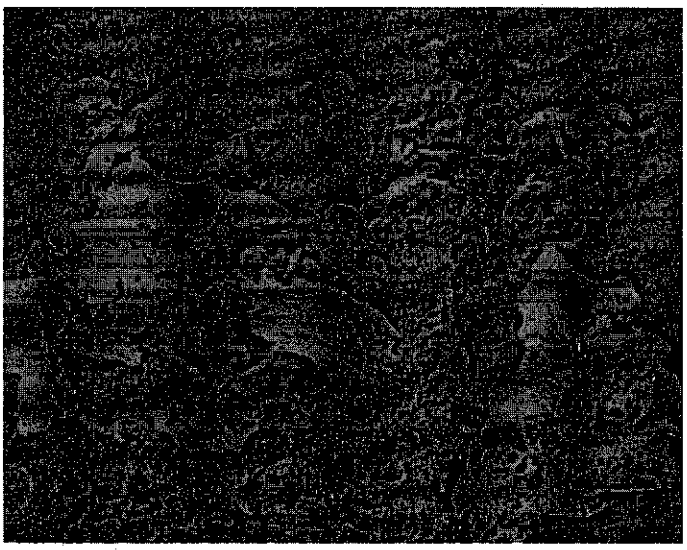


Figure 3: Scanning electron photomicrograph of a relatively "non macroporous" carbon granule. Area shown is 30 x 27 μ

CHAPTER 3
METHODOLOGY

3.1 Sample Preparation

These are the steps to produce activated carbon from rice husk in sequence:

(i) Sample Cleaning

The samples (rice husks) were first washed with distilled water to remove all the contaminants such as dust, small insects etc. Although it is quite impossible to remove all the contaminants from the rice husks, by minimizing it, the purity of the rice husks composition could be preserved.

(ii) Drying

After the rice husks were cleaned, they were put on a tray for the drying process. The importance of the drying phase is to remove all the volatile components and moisture content exist in the rice husks. The drying was carried out in oven for 12 hours with the temperature of 110 °C to ensure all the volatile components are successfully removed

(iii) Grinding

The purpose of grinding is to increase the specific surface area of the carbon. The grinder machine was at first set at the minimum (6 mm) which will produce coarse size of rice husks. Gradually the grinder setting was gradually increased to get finer size of rice husks. It is important to set the grinding size range and timing appropriately to prevent too many rice husks to become too

fine or worse, become dust. This is because the size range desired for the sample is only between 2mm- 250 μm.

(iv) Sieving

The sizes of the sieve chosen for characterization process were 1 mm- 2mm, 500μm – 1mm and 250 μm - 500μm. The sieving time was set at 10 minutes for each batch to ensure the precision of the size characterization.

(v) Sampling and Acid Dilution

The sieved rice husks were firstly stored in different container indicating its sizes. (1 mm-2mm, 500μm–1mm and 250 μm-500μm). The acid dilution steps are to prepare the acids for the rice husks activating process. Three different concentrations (2 mol, 10 mol, and 14.4 mol) of nitric acid were prepared by dilution of 65 wt% nitric acid.

(vi) Activation/Digestion

The activating agent used was nitric acid. The activation process was conducted based on specific parameters which have been decided earlier. The parameters varied for the experiments are particle size, activating agent concentration and the activating time. Variation of nitric acid concentration (2 mol, 10 mol, and 14.4 mol) and activation time (4 hours, 12 hours and 24 hours) were used to activate the rice husks. For all activation process, the rice husks-acid ratio was set at 1:10. For example; 10 mg of rice husks are immersed with 100 ml of acids.

(vii) Washing

The digested rice husks were washed with excess distilled water to neutralize the pH of the rice husks. The vitality of this step is to stop the acid digestion at the respective time that has been located earlier. The pH is checked by using the pH meter.

(viii) Sample Drying

After being washed, the rice husks were placed in an oven for 3 hours at temperature 110 °C. This is to remove the moisture content before the samples are taken to the furnace for carbonization process.

(ix) Carbonization

For the purpose of the rice husks carbonization, the dried rice husks were placed in close crucibles with the parameters labeled accordingly. The rice husks were carbonized in two batches. The first batch was carbonized at 700°C while the second batch was carbonized at 500 °C, both for two hours.
As a safety precaution, once the carbonization times were completed, the furnace was set back to 30 °C to allow the furnace to be cooled down to room temperature. The samples were taken out from the furnace only when the furnace was cool enough.

3.2 Sample Analysis

After the sample is prepared, analysis steps on the sample will be conducted which are:

(i) Preparation of Standard Solution

The concentration of the standard solution is prepared to be within the range 20 to100 ppm. This standard solution is very important since the standard solution curve obtained from the Atomic Adsorption Spectroscopy is very crucial. Besides, the same standard solution will be used in adsorption stage.

(ii) Adsorption Steps

The adsorption steps were carried out by shaking 0.1 g sample (rice husks) with 25 ml of the Fe(II) ion solution from 5 -100 ppm in conical flasks. The samples were shaken for 24 hours. The purpose of shaking the sample is to allow the adsorption process to achieve equilibrium phase. The samples were then filtered for the filtrates to be analyzed.

(iii) Adsorption Analysis

The filtrates were analyzed spectromatically using Atomic Absorption Spectrometer (AAS). All experiments were carried out at room temperature.

CHAPTER 4
THEORY

4.1 Carbon Adsorption

Adsorption is the concentration of a solute at the surface of a solid. This phenomenon takes place when such a surface is placed in contact with a solution. A layer of molecules of solute accumulates at the surface of the solid due to imbalance of surface forces [8].

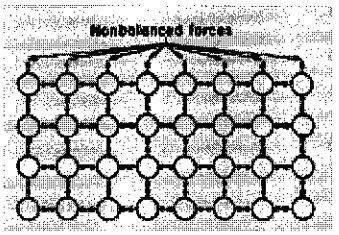


Figure 4: Representation of forces in a solid

In the interior of the solid, molecules are completely surrounded by similar molecules and therefore subjected to balanced forces, as indicated by the arrows in Fig.4. Molecules at the surface are subjected to non balanced forces. Because these residual forces are sufficiently strong, they may imprison molecules of a solute with which the solid is in contact. This phenomenon is called physical (or van der Waals) adsorption. The solid (e.g. activated carbon) is termed the adsorbent and the solute being adsorbed is the adsorbate. Adsorption capacity is directly related to the total surface of adsorbent since the larger this surface is, the more residual (unbalanced) forces are available for adsorption. [8]

4.1 Adsorption Isotherms

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms (Langmuir, Freundlich, and BET). Adsorption equilibrium is established when the concentration of contaminant remaining in solution is in dynamic balance with that at the surface of the solid [8]. It is much affected with the pH, temperature, and other parameters upon the adsorption process.

4.1.1 Langmuir Isotherm

In the development of the Langmuir isotherm, it is assumed that the solute is adsorbed as a monomolecular layer at the surface of the adsorbent. Langmuir isotherm is developed based on four important assumptions as follows:

(i) Adsorption occurs at definite localized sites on the surface
(ii) Each site can bind only one molecule of the solute
(iii) The energy of adsorption (strength of the bond) is the same for all sites
(iv) There are no forces of interaction between adjacently adsorbed molecules

This is the most often used adsorption isotherm, being given by the relationship

$$X/M = KbC_e / (1+KC_e)$$

Where;

X = weight of solute adsorbed (adsorbate, mg)
M = weight of adsorbent (g)
K = the equilibrium constant (cm^3 of adsorbent/mg of adsorbate)
C_e = the equilibrium concentration of solute (mg/liter)
b = a constant which represents the monolayer coverage per unit weight of adsorbent (mg of adsorbate / g of adsorbent).

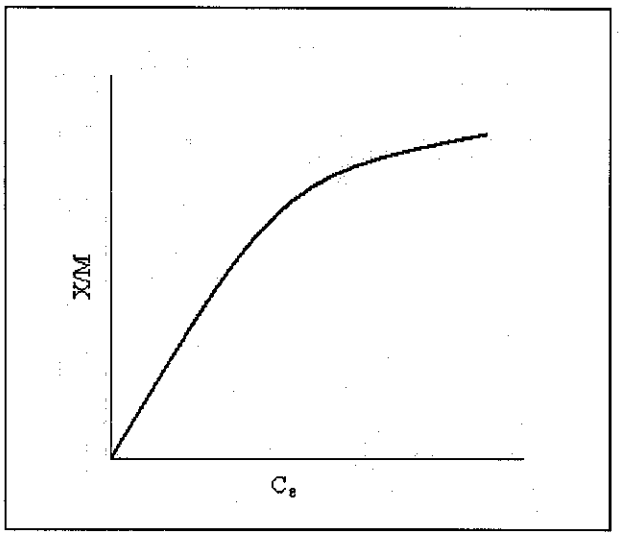


Figure 5: Langmuir isotherm

The equation can be rewritten in linear form by taking the reciprocal of both members:

$$1/(X/M) = (1/Kb)\ (1/C_e) + (1/b)$$

A plot of $1/(X/M)$ versus $1/C_e$ yields a straight line, which permits determination of parameters K and b from its slope and ordinate intercept, respectively [8].

4.1.2 Freundlich Isotherm

Freundlich Isotherm is the most widely used mathematical expression of adsorption in aqueous systems. The Freundlich isotherm is expressed by the equation;

$$X/M = kC_e^{1/n}$$

X/M and C_e have the same meaning as in Langmuir's isotherm, and k and n are constants dependent on several environmental factors. In linear form, the equation is re-written by taking logarithm of both members:

$$\log (X/M) = (1/n) \log C_e + \log k$$

a logarithmic plot of X/M versus C_e yields a straight line, which permits determination of parameters n and k from its slope and ordinate intercept at $C_e = 1$ [8].

4.1.3 BET Adsorption Isotherm

The most common method for determining the surface area of activated carbon and other porous adsorbents is Brunauer, Emmet, and Teller (BET) method. The BET model assumes that layers of molecules are adsorbed on top of the previously adsorbed molecules. Each layer adsorbs according to the Langmuir model. The BET isotherm is expressed by the equation

$$\frac{X}{M} = \frac{bkC_e}{(C_s - C_e)[1 + (k-1)C_e / C_s]}$$

The constant b has the same meaning as in the Langmuir isotherm, and k is a constant related to energy of adsorption. C_s is the concentration of solute at saturation of all layers.

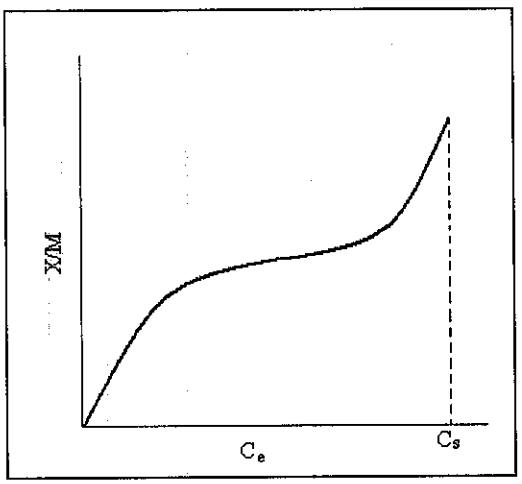


Figure 6: Plot of Isothermal adsorption data following BET model

A plot of isothermal adsorption data, following BET model, results in an S-shaped curve where the value of C_s can be estimated [8]. The equation can be linearly arranged as:

$$\frac{Ce}{(Cs - Ce)(X/M)} = \frac{1}{Kb} + \left(\frac{k-1}{kb}\right)\left(\frac{Ce}{Cs}\right)$$

A plot of $C_e/ (C_s-C_e) (X/M)$ versus C_e/C_s should yield a straight line. Constants k and b can be estimated from the slope and ordinate intercept of this line. The value of C_s estimated can be adjusted so that a good linear fit is obtained [8].

4.3 Adsorption Operation and Breakthrough Curves

In practice, adsorption in activated carbon is conducted either as a batch or continuous operation. In batch operation, powdered activated carbon is mixed with the wastewater and allowed to settle. Continuous operation is performed in columns containing granular carbon (40-80 mesh) [8]. It is more economical than batch operation and has found the widest application. Removal of contaminants in activated carbon columns occurs by three mechanisms: (1) adsorption, (2) filtration of large particles (3) partial deposition of colloidal material. Percent removal depends primarily on contact time between wastewater and activated carbon [8].

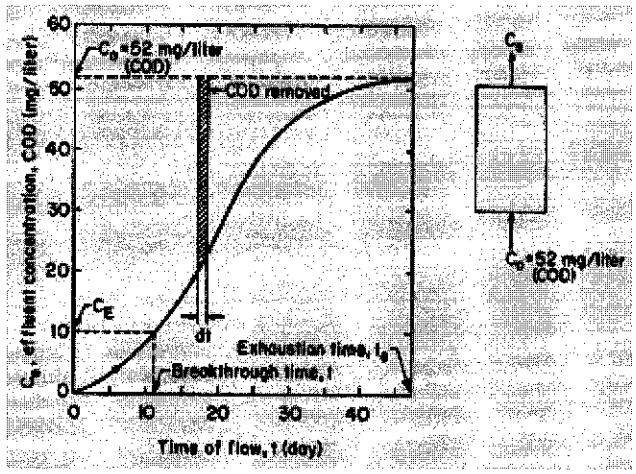


Figure 7: Typical Breakthrough curve for activated carbon adsorption

When a wastewater flows through an activated carbon column, contaminants are gradually removed and the wastewater becomes progressively purified as it moves through the column. There is no sharp demarcation between the purified wastewater and the feed. Instead a transition zone is formed in which the contaminant concentration varies from a maximum at the back of the zone to nearly zero at the front of the zone. This zone is the active portion of the column and is termed adsorption zone [8]. The forward movement of this adsorption zone can be seen by plotting the so-called breakthrough curves. The ordinate of a breakthrough curve is the effluent concentration, e.g. in COD, mg/liter, and the abscissa is time of flow through the column, e.g. days of flow. The abscissa is also frequently expressed in terms of bed volumes of total flow e.g. thousands of bed volumes [8].

Ordinarily, one does not operate an adsorption column until exhaustion in the case of the column in fig. one may decide to stop the operation when the effluent concentration reaches a value C_E = 10 mg/liter COD. This concentration C_E is referred to as breakthrough concentration [8].

CHAPTER 5
RESULTS AND DISCUSSIONS

5.1 Characterization of Adsorbent Material

Based from previous studies on rice husk by Rahman, Ismail and Osman, the composition of rice husks are as follows [9]:

Composition (%)	Sample			
	Raw husks	Digested 4h	Digested at 10 h	Digested at 12h
Silica	16.1	63.0	74.0	74.0
Cellulose	35.5	24.0	23.0	22.8
Hemicellulose	22.3	7.1	3.0	3.1
Lignin	13.6	6.1	1.9	0.2
Solubles & Moisture	12.5	-	-	0
Total	100	100.2	101.9	100.1

Table 1: Composition of organic constituents in the digested husks as compared to the raw husks

The raw husks composition showed that it is mainly consist of organic materials i.e. cellulose, hemicellulose and lignin. It can be observed that after 4 hours of digestion, hemicellulose and lignin are readily digested by the nitric acid where the reaction was vigorous and exothermic with overall mass loss of about 68 – 74 %. After 10 hours of digestion, the amount of hemicellulose and lignin are 3.0 and 1.9 % respectively. After 12 hours, a trace of lignin that is only 0.2 % was detected while hemicellulose content remained almost unchanged. Cellulose, compared to hemicellulose and lignin was digested at slower rate. Even after 12 hours of digestion with the nitric acid, the cellulose still remained 23%. The resistant of hemicellulose is due to its crystalline nature [9].

Among the materials in the rice husks, silica is found to be almost insoluble in nitric acid. The increase in silica content with the time of digestion was solely due to the reduction in overall mass after digestion. As the husks contain silica and organic

materials, it is therefore expected that Fe(II) ions will be mostly adsorbed either by silica or carbonaceous material or by both components [9]

5.2 Adsorption Studies

5.2.1 Effect of Activating Agent (nitric acid) Concentration

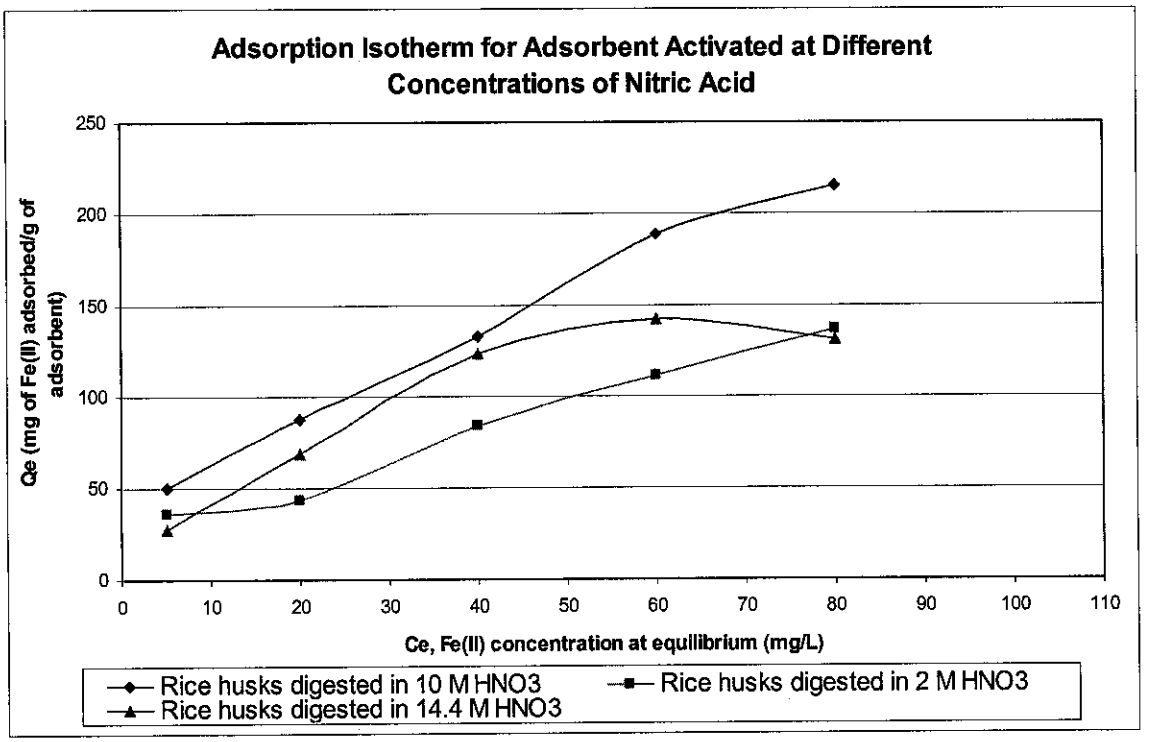


Figure 8: Adsorption isotherms on adsorbents produced at different concentrations of activating agent

In order to evaluate the effect of activating agent concentration, the adsorption experiment was done on the husks that are activated by three different nitric acid concentrations which is 2 M, 10 M and 14.4 M at constant activation time (12 hours), carbonization time and carbonization temperature. The results illustrate that husks with higher activating concentration has higher Fe(II) ions uptake. From the results, it could be observed that the highest Fe(II) ions uptake is 50 – 220 mg Fe(II)/g of activated carbon for the adsorbents prepared using 10 mol nitric acid compared to the adsorbents activated by 2 M nitric acid which yield from 35 – 140 mg Fe(II)/g of activated carbon. It indicates that higher activation concentration provides higher microporosity of the

adsorbents as increasing concentration of the activation agent increased the surface area and micropores volume. The activating agent acts to the raw rice husks by two phase. Initially, when the activation agent is poured to the raw material, the micropores started to form. The next phase is the pore widening, which results from the chemical effect of the activating agent inside the open pores. Thus it could be concluded that the adsorbent produced by higher activating concentrations yield better adsorption uptake.

However for the adsorbents activated by the highest concentration of nitric acid which is 14.4 M, the Fe(II) uptake is lesser. It can be observed that the Fe(II) uptake is in the range of 25 - 130 mg Fe(II)/g of activated carbon. The decrement of adsorption capability is predicted to be because of too high activating agent concentration which caused destructions of the microporous structure of the activated carbon. When this happened, the activated carbon structures will disintegrate and break. Therefore the activated carbon will have less mechanical strength to withstand the adsorption process

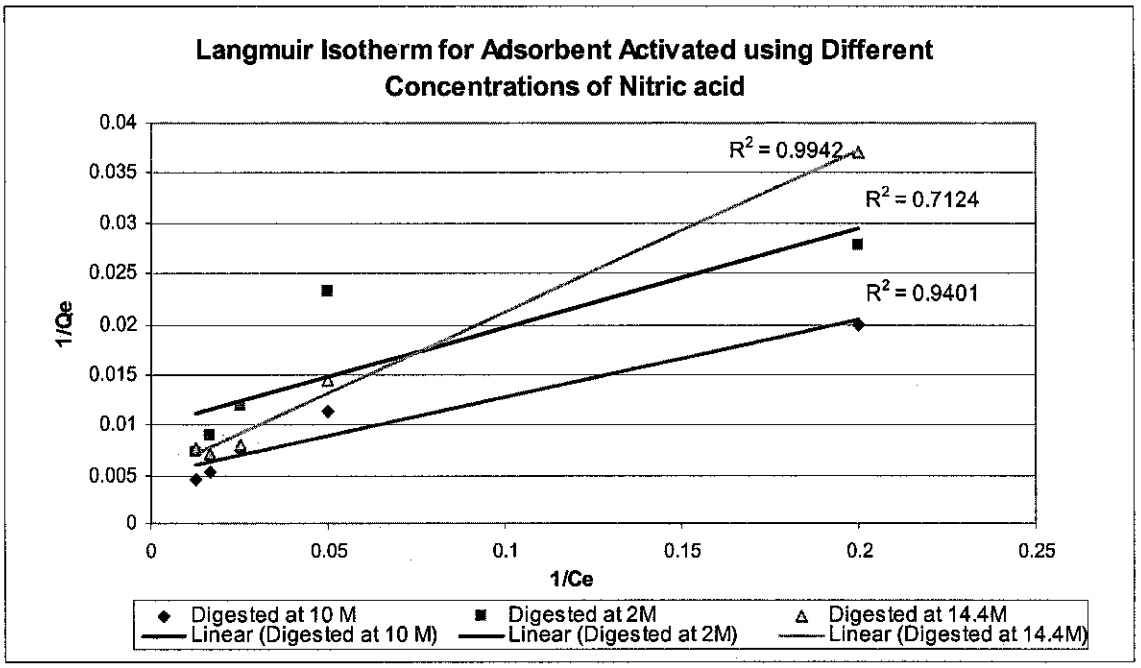


Figure 9: Langmuir isotherm for adsorbent activated using different concentrations of Nitric acid

The adsorption characteristics of adsorbate onto the adsorbent were characterized using the Langmuir model which has been explained in the previous chapter. From Figure 9,

the samples digested by 14.4 M nitric acid gives the highest R^2 value which is 0.9942 followed by samples digested by 10 M acid, 0.9401 and samples digested by 2 M acid, 0.7124. Thus it can be stated that the entire sample obey the Langmuir isotherm with the base characteristic assumption that only monolayer adsorption take place. Therefore, it could be concluded that the sample digested by 10 M nitric acid which has the highest Fe(II) ion uptake and fits the Langmuir isotherm is the most favorable adsorbent.

5.2.2 Digestion Time Effect

The physical appearance of rice husks after been digested with nitric acid are notably difference from that of the raw rice husks. The sizes of the rice husks particle decreases with increase of digestion time. From the original color of the raw rice husks which is dark brown, the color changed significantly to yellowish, light yellow and white, dependent on the digestion time. It could be observed that after 24 hours of digestion, the husks have been reduced to a white powdery form. At this stage the sample consist of a finely degraded cellulose-silica skeleton which contains about 26% cellulosic material and 74% silica with trace amount of lignin [9].

After 12 hours of digestion, surface area of the husks has increased by about 60 times and thus created the largest internal surface area or a maximum porous structure [10]. Thus the residue after 12 hours digestion consists of a highly porous cellulose-silica composite [9].

Although 24 hours digestion time provides more porous structure of carbon, the carbon structure is already too porous where the mechanical strength of the structure started to decrease that make it unable to carry out the adsorption uptake. Consequently the activated carbon structure will collapse.

5.2.3 Carbonization Effect

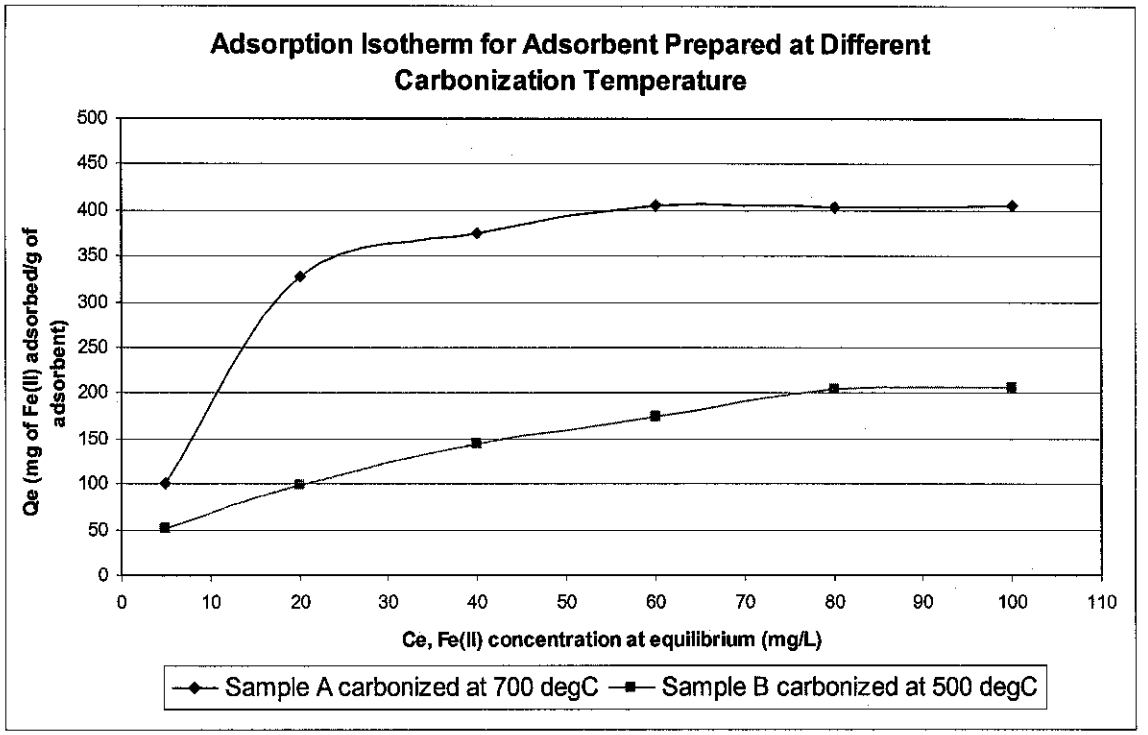


Figure 10: Adsorption isotherms on adsorbents treated at different carbonization temperatures

To study the effect of carbonization on the adsorption process, the carbonization temperatures were varied at 700°C and 500°C by keeping other parameters constant. Figure 10 shows the adsorption isotherms. It can be observed that the adsorption capacity increased with increasing carbonization temperature from 500 °C to 700 °C. The adsorbent carbonized at temperature at 700 °C has the higher adsorption capacity in the range of 100-405 mg Fe(II)/g of activated carbon. For the adsorbent carbonized at temperature 500 °C, the adsorption capacity was varied from 50 - 200 mg Fe(II)/g of activated carbon for the same condition. So it can be concluded that 700 °C is the optimum carbonization temperature where at this temperature the specific area of the activated carbon is the largest.

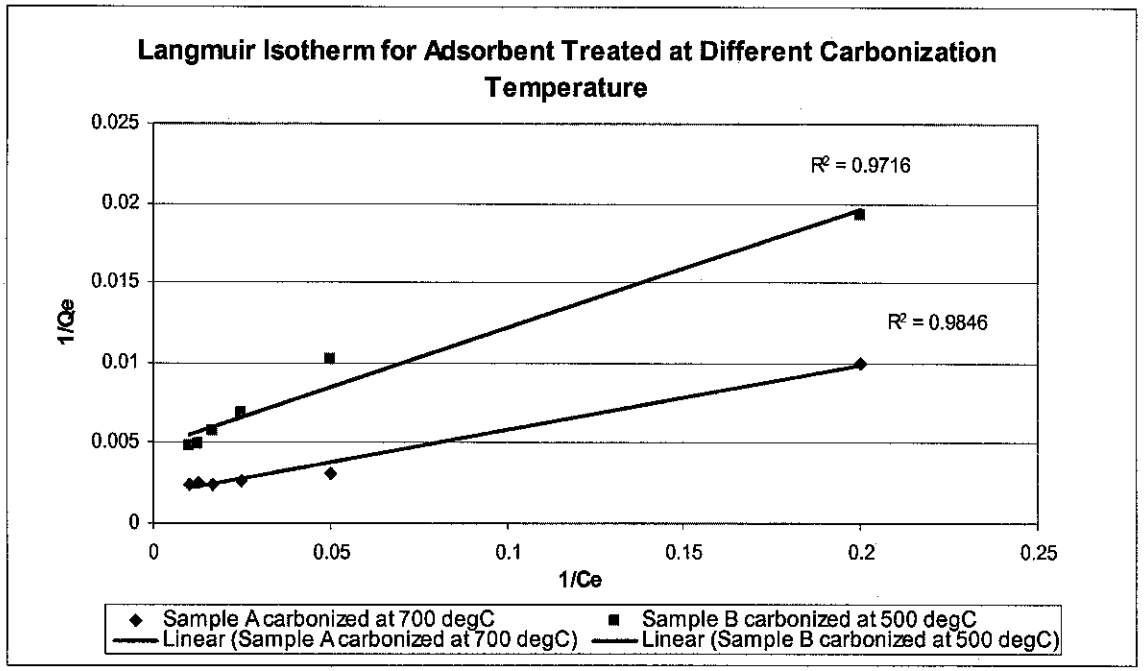


Figure 11: Langmuir isotherms on adsorbents treated at different carbonization temperatures

Using the Langmuir model, it is observed that the sample carbonized at 500 °C has the R^2 value of 0.9716 while the sample carbonized at 700 °C has the R^2 value of 0.9846. Therefore the most favorable adsorbent is the sample carbonized at 700 °C because it has the highest adsorption capacity and fits the Langmuir isotherm.

By carbonizing the rice husks, more pores are formed as a result of thermal decomposition of cellulosic materials. Although the basic microstructure of the carbon was formed at 500 °C, some pores are blocked by the pyrolysis products and could be available when higher temperature treatment is given. In addition, lower carbonization temperature provides lower volatilization, hence less non-carbon species eliminated [10]. However, at temperature higher than 700 °C, the structure of carbon will start to degrade thermally due to the intense heat applied to it. Thus it will leads to the destruction of the husks micropores which will results to the reduction of the specific surface area that will also diminish the adsorption capacity.

According to Rahman, Ismail and Osman, the adsorption patterns do not reflect the change in silica contents of the samples. After the carbonization process, the materials with larger proportion of silica are produced (SiO_2 80%), thus increased the adsorption activities compared to the husk's condition before carbonization which contains less silica. Therefore, the formation of the surface complexes which is most likely related to predominant silica content of the samples, can be presented as follows

$$2(\equiv Si\text{-}OH) + Fe^{2+} \leftrightarrow (\equiv SiO^{-})_2 2Fe^{2+}$$

So it could be concluded that the Fe(II) ions are preferentially adsorbed on the silica surface rather than on the cellulosic materials [9].

5.2.5 The Effect of Solution PH and Shaking Time

Due to time constraint, the experiments on the effect of Fe(II) solution pH and the shaking time were unable to be carried out. However the effects of these two parameters are discussed based on the literature review.

PH Effect

The extent of Fe(II) adsorption increases with increases of pH of the solution, but decreases at certain point of higher pH. The maximum adsorption seems to be related to the hydrolysis and precipitation of the metal ions as reported by several researchers [9]. The maximum adsorption seems to be related to the hydrolysis and precipitation of the metal ions. It was also agreed that the adsorption of metal ions at the solid-solution interface was controlled by the formation of the surface complexes between the free metal ions and the deprotonated sites [9].

Effect of Shaking Time

Generally, the increased shaking time improve the adsorption capability of the adsorbents. Longer shaking time permits higher opportunity for the adsorbents and the Fe(II) ions to collide with each other. Sufficient contact time between the adsorbents and Fe(II) ions is important for the process to reach equilibrium.

CHAPTER 6
CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

Higher concentrations of the agent used in activating the rice husks increased the adsorption capacity of the adsorbent produced. Higher activation concentration imparts higher microporosity of the adsorbents as the concentration increment of the activation agent provides more surface area and micropores volume. As a result, the adsorbent produced by higher activating concentrations yield better adsorption uptake. Longer digestion time also created larger internal surface of the carbon; hence allows more adsorption uptake. The optimum digestion time is approximately 12 hours where longer digestion period than 12 hours could initiate the destruction of the carbon structure which will decrease the adsorption capability of the carbon.

In order to get maximum adsorption uptake, the carbonization temperature should be controlled at the optimum point in the range of 600 °C– 700 °C for the carbon to obtain high specific area. While the basic microstructure of the carbon was formed at lower temperature, the volatilization rate is still low where the carbon pores are still blocked by the pyrolysis products. Intense heat from higher temperature above the optimum range will cause thermal degradation of the carbon which will destroy it. Higher proportion of silica in the activated carbon resulting from the carbonization process increases the adsorption rate where Fe(II) ions are preferentially adsorbed on the silica rather than on the cellulosic material.

As a conclusion, rice husk activated carbon is identified as a potential adsorbent for metal removal. As a consequence, further works and researches need to be done in order to increase or commercialize rice husks applications in industry especially in the wastewater treatment.

6.2 Recommendations

Due to constraints of time and the unavailability of the major equipment, several other parameters which may affect the adsorption capability of the activated carbon produced are unable to be carried out. It is recommended to further the research on the effect of different particle size of the rice husks. Theoretically, smaller particle could increase the contact surface area between the metal ions and the adsorbent which will increase the adsorption uptake. On the other hand, maybe smaller particles of rice husk is more likely to be degraded compared to the larger particles during the preparation steps to convert it to activated carbon.

A further study specifically on the effect and the chemistry of Fe(II) ions on the carbon surface is recommended, for example the effects of deprotonated carbon surface and SiOH groups towards the Fe(II) adsorption. In addition, the ability of the activated carbon to adsorb common metals exist in the wastewater streams such as chromium, lead etc. should also be investigated.

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APPENDICES

Simplified Experiment Results

Activation with different concentration of nitric acid

[illegible]	
concentration at equilibrium (ppm) (Ce)	mg copper/g of adsorbent (Qe)
5	50
20	88
40	133
60	189
80	215

[illegible]	
concentration at equilibrium (ppm) (Ce)	mg copper/g of adsorbent (Qe)
5	36
20	43
40	84
60	111
80	137

14.4 mol	
concentration at equilibrium (ppm) (Ce)	mg copper/g of adsorbent (Qe)
5	27
20	69
40	124
60	142
80	131

For carbonization temperature of 700 °C and 500°C

[illegible]	
concentration at equilibrium (ppm) (Ce)	mg copper/g of adsorbent (Qe)
5	52
20	98
40	144.5
60	175
80	204.9
100	206

700 deg C	
concentration at equilibrium (ppm) (Ce)	mg copper/g of adsorbent (Qe)
5	100
20	328
40	375
60	406
80	404.3
100	405.8

Undergone Milestone for One Semester Final Year Project

No	Detail / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	**Selection of Project Topic**																				
	~ Propose Topic																				
	~ Topic assigned to student																				
2	**Preliminary Research / Design Work**																				
	~ Introduction																				
	~ Objective																				
	~ List of references / literature																				
	~ Project planning																				
	~ Identify related lab equipment																				
3	**Submission of Preliminary Report**			●																	
	(Initial Proposal)																				
4	**Project Work**																				
	~ List of References / Literature																				
	~ Lab Equipment and Apparatus																				
	~ Sample Preparation																				
	~ Practical / Laboratory Work																				
5	**Submission of Progress Report**																				
	~ First Draft										●										
	~ Submission of Progress Report											●									

6	**Project Work continue**	
	~ List of References / Literature	
	~ Lab Equipment and Apparatus	
	~ Sample Preparation	
	~ Practical / Laboratory Work	
7	**Submission of Dissertation Draft**	
8	**Submission of Project Dissertation**	
9	**Oral Presentation**	

Suggested milestone

Process